**SN AND (OR) W SKARN AND REPLACEMENT DEPOSITS**
**(MODELS 14a-c; Cox, 1986; Reed and Cox, 1986; Reed, 1986)**

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## SUMMARY OF RELEVANT GEOLOGIC, GEOENVIRONMENTAL, AND GEOPHYSICAL INFORMATION

See general comments in section entitled "Introduction" in CU, AU, ZN-PB skarn deposits model (Hammarstrom and others, this volume).

### Deposit geology

These deposits consist of tin, tungsten, and beryllium minerals in skarns, veins, stockworks, stratabound replacement deposits, and greisens in carbonate rocks at or near granite contacts.

### Examples

Tungsten skarns: Pine Creek Mine, Calif.; Mill City district, Nev.; Rock Creek district, Mont.; Mactung, Northwest Territories, Canada.
Tin skarns: Lost River, Alaska; Moina, Tasmania, Australia.
Tin replacement deposits: Renison Bell, Tasmania, Australia; Dachang, Guangxi, China.

### Spatially and (or) genetically related deposit types

Associated deposit types (Cox and Singer, 1986) include zinc skarns (Model 18c), tin greisens (Model 15c), and quartz-cassiterite-sulfide mineral veins, quartz-tourmaline-cassiterite veins, and (or) tin-tungsten-molybdenum stockworks (Model 15b). See Vein and greisen SN and W deposits model (Elliott and others, this volume).

### Potential environmental considerations

These deposits have low acid drainage generation potential relative to many other deposit types because of their generally low sulfide mineral content, relatively small deposit size, low impact mining and milling methods (relative to many other mineral deposit types), and abundance of associated carbonate rocks, which can buffer any acid drainage generated as a consequence of sulfide mineral oxidation. However, some tin replacement deposits and some tungsten skarns (for example, Mactung, Cantung; Canada) have sulfide-mineral-rich zones that may have significant acid generation potential. Both tungsten and tin are present along with fluorine and beryllium in some skarn deposits.

### Exploration geophysics

In exploration, geophysics is principally used to define associated highly differentiated leucogranites by their relatively weak magnetic response, low density, and high radioelement content (Hoover and Knepper, 1992). Magnetic and induced polarization surveys can be used to outline the surface projection of orebodies because magnetite, pyrrhotite, and other sulfide minerals are common in these deposits. Although skarns typically have a positive density contrast relative to adjacent intrusions and carbonate rocks, gravity surveys are not commonly used due to their relatively high cost and non-specificity for ore. Remote sensing techniques can effectively identify carbonate terranes and iron enrichment in skarns if skarn is exposed. In some cases, contacts between intrusions and sedimentary rocks can be mapped and carbonate rocks can be distinguished from non-carbonate rocks.

### References

Geology: Hepworth and Zhang (1982), Cox (1986), Reed (1986), Reed and Cox (1986).
Environmental geology: Sainsbury and others (1968).

## GEOLOGIC FACTORS THAT INFLUENCE POTENTIAL ENVIRONMENTAL EFFECTS

### Deposit size

Menzie and Reed (1986a,b) and Menzie and others (1992) present the following deposit size ranges, in millions of tonnes (tonnes=1 metric ton=1.102 short tons), expressed as percentiles of tonnage, for populations of N deposits:

| | | | |
|---|---|---|---|
| W skarns (N=36)- | 0.04 (90th percentile) | 0.80 (50th percentile) | 18 (10th percentile) |
| Sn skarns (N= 4)- | 1.6 (90th percentile) | 9.4 (50th percentile) | 58 (10th percentile) |
| Replacement Sn (N=6)- | 1.0 (90th percentile) | 5.2 (50th percentile) | 27 (10th percentile) |

The 50th percentile value is the median deposit size for each population. Most recent world production has been from relatively large deposits (10 million metric tons or more). The strategic mineral value of tungsten led to government subsidized mining of many small deposits (on the order of 1 million t or less) during World Wars I and II and the Korean War primarily in the western United States.

Host rocks

These deposits are hosted by carbonate rock, including limestone, dolomite, marble, and carbonate-bearing pelite, argillite, and shale. In terms of Glass and others' (1982) classification of bedrock types, most host rocks for these deposit types are type IV, that is, they are highly calcareous sedimentary rocks or metamorphosed calcareous sedimentary rocks that have extensive buffering capacity.

Surrounding geologic terrane

These deposits are typically associated with contact zones around relatively evolved granite stocks, plutons, or batholiths; cogenetic volcanic rocks are generally absent.

Wall-rock alteration

Wall-rock alteration commonly includes extensive greisen development and sericitic and silicic alteration (Kotlyar and others, 1995). Intrusive rocks associated with tungsten skarns may be altered to an endoskarn assemblage, which consists of mica, calcite, and pyrite.

Nature of ore

Tungsten skarn orebodies are stratiform deposits that can extend for hundreds of meters along lithologic contacts. Stockwork and local crosscutting veins are common. The grain size and molybdenum content of scheelite in tungsten skarns varies. Paragenetically early, anhydrous skarn generally contains relatively fine-grained, high-molybdenum scheelite, whereas retrograde skarn contains medium to coarse grained low-molybdenum scheelite. Coarse grained, vuggy skarn with uneven ore grades forms from impure marble; finer-grained, compact skarns with more evenly distributed ore grades tend to form from pure marbles (Einaudi and others, 1981).

Cassiterite in tin skarns is commonly very fine grained. Tin concentrations range from 0.1 to 1 weight percent in deposits that include 10 to 90 million tonnes of ore. Tin may contained in silicate minerals, including garnet and hornblende (Eadington, 1983).

Deposit trace element geochemistry

W skarns- W, Mo, Zn, Cu, Sn, Bi, As, Fe, Mn.
Sn skarns- Sn, W, F, Be, Zn, Cu, Ag, Li, Rb, Cs, Re, B.
Replacement Sn- Sn, As, Cu, B, W, F, Li, Pb, Zn, Rb.

See tables 1-4 for examples of ranges of geochemical signatures associated with rock, stream sediment, and soil samples from these deposit types; also see Beus and Grigorian (1977) for additional trace element data pertaining to these deposits.

Ore and gangue mineralogy and zonation

Skarn deposits exhibit temporal and spatial zoning that reflect stages of skarn development. Early formed prograde mineral assemblages are overprinted and crosscut by retrograde mineral assemblages to varying degrees. Initial metamorphism forms marble and hornfels. Subsequent metasomatism forms high-temperature anhydrous calcsilicate minerals that may be overprinted or cut by later, lower temperature hydrous mineral assemblages. Although the principal ore minerals in tungsten and tin deposits are generally not sulfide minerals, a variety of sulfide minerals can be present in these deposits. Sulfide minerals are generally deposited with late hydrous minerals.

In tungsten skarns, scheelite is deposited near the marble front during early prograde metasomatism but is generally remobilized and redeposited in coarse-grained, high-grade masses with sulfide minerals in zones of hydrous alteration. In tungsten-tin skarns, tungsten is concentrated proximal to intrusive rock, whereas tin is concentrated in more distal parts of skarns (for example, Shizhuyuan, China). In some cases, sulfide minerals are present close to intrusive contacts (for example, Black Rock, Calif.).

Tin skarns may be calcic or magnesian. Calcic tin skarns may be enriched in magnetite. Cassiterite is concentrated residually in oxidized parts of lode deposits, especially if deposited with sulfide minerals. In tin skarns, tin may be present in titanite (sphene), andradite, and grossular. Many other tin silicate, sulfide, and borate minerals

**Table 1.** Summary ranges of analytical data for 20 samples of skarn from the Lentung W skarn deposit, Rock Creek district, Mont. (data from DeBoer, 1991).

[Samples represent garnet-pyroxene skarn ± scheelite and chalcopyrite. Methods include DCP, ICP, AA, INAA for W. Sn was analyzed, but not detected in any of the samples. Concentrations reported as ppm, unless otherwise indicated. N= number of samples in which the element was detected. See DeBoer (1991) for detection limits and details of analyses; --, not detected]

| Element | N | Minimum | Maximum | Mean |
|---|---|---|---|---|
| Au (ppb) | 1 | 11 | 11 | 11 |
| Ag | 18 | .5 | 151 | 10.4 |
| Al ( %) | 20 | .2 | 224 | 13.7 |
| As | 13 | 7 | 55 | 36 |
| Ba | 20 | 1 | 212 | 25 |
| Be | 11 | 0.6 | 6.5 | 2.5 |
| Bi | 16 | -- | 130 | 31 |
| Ca (%) | 2 | 4.32 | 7.44 | 5.88 |
| Cd | 4 | 1 | 21 | 9 |
| Ce | 20 | 7 | 153 | 91 |
| Co | 20 | 4 | 54 | 18 |
| Cr | 20 | 10 | 237 | 82.2 |
| Cu | 20 | 2 | 6,005 | 411.4 |
| Fe (%) | 8 | 2.08 | 9.74 | 6.17 |
| Ga | 14 | 3 | 25 | 12 |
| Hg (ppb) | 20 | 15 | 50 | 22 |
| K (%) | 4 | .05 | 0.65 | 0.32 |
| La | 13 | 2 | 114 | 28 |
| Li | 20 | 3 | 49 | 12 |
| Mg (%) | 19 | .13 | 6.12 | 2.32 |
| Mn | 18 | 1,868 | 19,460 | 8,610 |
| Mo | 20 | 8 | 1,214 | 176 |
| Na (%) | 20 | .1 | 2.26 | 0.33 |
| Nb | 20 | 5 | 44 | 14 |
| Ni | 20 | 15 | 59 | 42 |
| Pb | 15 | 4 | 11,100 | 798 |
| Rb | 6 | 33 | 642 | 286 |
| Sb | 14 | 6 | 42 | 18 |
| Sc | 16 | 26 | 133 | 70 |
| Sr | 20 | 8 | 626 | 86 |
| Ta | 20 | 28 | 230 | 114 |
| Th | 15 | 11 | 55 | 28 |
| Ti (%) | 19 | .02 | 0.65 | 0.22 |
| V | 20 | 17 | 352 | 144 |
| W | 18 | 15 | 3,200 | 620 |
| Y | 20 | 4 | 46 | 19 |
| Zn | 20 | 16 | 954 | 183 |
| Zr | 20 | 13 | 229 | 106 |

have been identified in skarns; stannite ($Cu_2FeSnS_4$) is the most important of these.

In the tungsten-tin-fluorine calcic skarns at the Mt. Lindsay deposit (Tasmania), sulfide skarn with low tin content formed near the contact between carbonate rocks and igneous rocks. Cassiterite-rich magnetite skarn formed in the distal parts of the skarn near unreplaced marble. During intermediate stages of skarn formation, cassiterite reacted completely to produce tin-bearing silicate minerals such as titanite, amphibole, and ilvaite (Kwak, 1983).

W skarns: Prograde- Pyroxene (diopside-hedenbergite), garnet (grossular-andradite), idocrase, wollastonite.
Retrograde- Spessartine-rich garnet, biotite, amphibole, plagioclase, epidote, quartz, chlorite, sulfide minerals (chalcopyrite, pyrite, pyrrhotite, sphalerite, bornite, arsenopyrite, bismuthinite), magnetite, fluorite, native bismuth.
Ore- Scheelite, molybdenite, wolframite, cassiterite.

**Table 2.** Summary ranges of analytical data for samples of skarn, endoskarn, hornfels, marble, and jasperoid associated with skarn in the Tonopah 1°x2° quadrangle, Nev.
[Concentrations reported as ppm; N, number of samples in which element was detected; detection limits for each element are given in parentheses. Unpublished emission spectrographic data for rock samples from Lodi Hills, Ellsworth, Cedar Mountain, Peg Leg Mine (San Antonio Mountains), Timblin Canyon in the Toiyabe Range, and the Victory W mine; D.A. John]

| Element | N | Minimum | Maximum | Mean |
|---|---|---|---|---|
| As (200) | 1 | 1,000 | 1,000 | 1,000 |
| Be (1) | 30 | 1 | 65 | 11 |
| Bi (20) | 6 | 10 | 500 | 143 |
| Cd (20) | 1 | 100 | 100 | 100 |
| Cu (5) | 27 | 5 | 7,000 | 356 |
| Mo (5) | 19 | 7 | 700 | 63 |
| Pb (10) | 38 | 10 | 20,000 | 1,054 |
| Sb (100) | 4 | 20 | 300 | 130 |
| Sn (10) | 16 | 10 | 200 | 56 |
| W (50) | 11 | 50 | 10,000 | 1,563 |
| Zn (200) | 14 | 200 | 10,000 | 2,686 |

**Table 3.** Summary ranges of trace element contents, in parts per million, for selected stream sediment samples from the Sn-W-Be district of the Seward Peninsula, Alaska (data from Sainsbury and others, 1968).
[Spectrograph and spectrophotometric data for 17 stream sediment samples from 13 drainages. N, number of samples in which the element was detected. See Sainsbury and others (1968) Table 1 for detection limits and Table 8 for descriptions of methods and samples]

| Element | N | Minimum | Maximum | Mean |
|---|---|---|---|---|
| As | 2 | 1,500 | 3,000 | 2,250 |
| B | 11 | 15 | 700 | 185 |
| Be | 12 | 3 | 160 | 45 |
| Cu | 17 | 7 | 150 | 34 |
| Li | 9 | 15 | 3,000 | 713 |
| Nb | 3 | 15 | 15 | 15 |
| Pb | 11 | 15 | 150 | 64 |
| Sn | 13 | 10 | 1,100 | 148 |
| W | 6 | 10 | 70 | 38 |
| Zn | 1 | 300 | 300 | 300 |

Sn skarns: Prograde- Idocrase, garnet (spessartine-rich grandite, tin-bearing andradite), malayite, danburite, datolite, pyroxene, wollastonite.
Retrograde- Amphibole, mica, epidote, magnetite, chlorite, tourmaline, fluorite, sulfide minerals (sphalerite, pyrrhotite, chalcopyrite, pyrite, arsenopyrite), Be minerals (helvite, danalite).
Ore- Cassiterite, scheelite.

Replacement Sn: Major minerals- Cassiterite, pyrrhotite, chalcopyrite, pyrite, arsenopyrite, ilmenite, fluorite.
Minor minerals- Pyrite, sphalerite, galena, stannite, tetrahedrite, magnetite.
Late veins- Sphalerite, galena, chalcopyrite, pyrite, fluorite.

**Table 4.** Summary ranges of trace element contents for soil associated with the Sn-W-Be district of the Seward Peninsula in the Lost River valley, Alaska (data from Sainsbury and others, 1968).
[Selected AA, spectrophotometric, and SQS for 40 soil samples. N, number of samples in which the element was detected. Li present, in undetermined amount, in 37 samples. See Sainsbury and others (1968) Table 9 for detailed description of samples and methods and Table 1 for detection limits. Minimum, maximum, and mean concentrations in parts per million]

| Element | N | Minimum | Maximum | Mean |
|---|---|---|---|---|
| As | 9 | 1,500 | 2,000 | 1,611 |
| B | 37 | 30 | 200 | 104 |
| Be | 32 | 2 | 270 | 74 |
| Cu | 40 | 16 | 610 | 92 |
| Nb | 32 | 0 | 30 | 19 |
| Pb | 40 | 35 | 2,100 | 448 |
| Sn | 37 | 10 | 1,500 | 210 |
| Zn | 40 | 50 | 5,000 | 1,074 |

Mineral characteristics

Tin ore at the Renison Bell, Tasmania, replacement tin deposit consists of fine-grained ( <150 micron) cassiterite closely associated with sulfide minerals (pyrrhotite, as well as minor chalcopyrite, pyrite, arsenopyrite, marcasite, sphalerite, and galena) in silicate-carbonate gangue.

Secondary mineralogy

Cassiterite, the primary ore mineral of tin, is very stable under most near-surface conditions and its dispersion is dependent more on physical than chemical conditions. However, cassiterite-plus-sulfide skarns in humid climates readily decompose, but cassiterite-quartz-tourmaline assemblages form residual soil overlying deposits. Oxidation can cause the formation of varlamoffite, a soft, earthy, impure hydrated stannic oxide that is less inert than cassiterite. Readily dissolved varlamoffite can release tin into solution.

Topography, physiography

Granitoid plutons associated with skarn tend to form positive areas of moderate to high relief. However, in semi-arid environments subjected to extended periods of weathering, some granitoid plutons may occupy topographic lows. Silicified rocks associated with skarns may form knobs or ridges.

Hydrology

Tungsten skarns are associated with largely unfractured plutons. Post-mineralization faults may focus ground water flow in underground workings.

Mining and milling methods

These deposits have been mined by open pit and underground methods.
W skarns: Mining method generally depends on the grade and form of the deposit; higher average ore grades (0.7 weight percent $WO_3$ or more) are generally required to warrant costs of underground mining operations. Underground methods include room-and-pillar (Cantung, British Columbia; King Island, Australia), cut-and-fill, stoping (Pine Creek, Calif.) or combinations of these methods (Anstett and others, 1985). Gravity, flotation, and chemical methods are used to produce natural and artificial scheelite, and ammonium paratungstate (APT) (Smith, 1994).

Scheelite concentrate has been produced in the United States using gravity, flotation, and magnetic separation techniques (Stager and Tingley, 1988). After crushing and grinding, sulfide minerals and scheelite are separated by flotation, and sulfide slimes are removed to tailings piles. Scheelite concentrates are processed to precipitate silica. Molybdenum is removed as $MoS_3$ via a precipitation process that releases $H_2S$ through scrubber-equipped stacks. An organic solvent extraction technique is used to produce APT.

Sn skarns: Cut and fill stoping methods are used at the Renison Bell, Tasmania, replacement tin deposit, the world's largest underground mine. Sulfide-mineral-rich and sulfide-mineral-poor ore are selectively stockpiled on the surface and blended ore is fed into a three-stage open crushing circuit that reduces ore from 750 mm to 15 mm. Ore is processed by flotation to remove sulfide minerals prior to gravity concentration of cassiterite (Morland, 1986). Staged grinding is used to liberate fine-grained cassiterite. Residual sulfide minerals in the gravity concentrate are removed by flotation. Cassiterite concentrates are leached with sulfuric acid to remove siderite, magnetic material is removed using magnetic separators; refined concentrates are then shipped to smelters. Tailings are combined with lime to adjust pH to 8.5 before being pumped to impoundments.

## ENVIRONMENTAL SIGNATURES

### Surface disturbance

Mining these deposits may result in associated open pits, tailings piles, and subsidence in areas of underground mining.

### Drainage signatures

The mobility of tungsten (probable aqueous species is $HWO_4^-$) is intermediate to low at normal pH. Tungsten is known to be present in aqueous solution in alkaline lakes.

W skarns: No data; most deposits studied in the Basin and Range do not have stream drainages. Water is probably well buffered by carbonate minerals but may contain elevated abundances of arsenic, zinc, molybdenum, tungsten, or uranium. Spring water discharged from a travertine spring terrace and Quaternary sand and gravel associated with tungsten skarns and epithermal manganese-tungsten deposits in the Rose Creek district, Pershing Co., Nev. contains as much as 0.3 weight percent $WO_3$ and 9 weight percent manganese, and has a pH of 6.4 and specific conductance of 2,690 micromhos (White and others, 1963, Table 23).

Sn skarns: Beryllium has not been detected in natural water of southwest Alaska where many of these deposits are present; tin abundances are also probably extremely low. Tin concentrations in fresh ground water and thermal water are $\leq 1$ $\mu$g/l; in oilfield brines, concentrations are as much as 670 $\mu$g/l (Forstner and Wittman, 1981). As demonstrated by hydromorphic dispersion anomalies associated with disseminated gold deposits in Nevada (Grimes and others, 1995), where ground water tungsten concentrations are 1 to 260 $\mu$g/l, tungsten can be mobile in ground water. However, the greatest tungsten concentrations are in samples for which Eh and arsenic speciation indicates reducing conditions associated with carbonaceous black shale host rocks.

### Metal mobility from solid mine wastes

Tungsten: No data.

Tin: The mobility of tin from cassiterite is generally low because cassiterite is very stable in the surface environment. Cassiterite is probably the principal tin phase in soil. Evolved granites associated with tin skarn and the skarns themselves contain elevated fluorine concentrations because of their fluorite abundances. In the granitic terranes of India, high fluorine abundances in water and soil are associated with the incidence of fluorosis in humans and livestock (Karunakaran, 1977). Although most public water supplies in the United States are fluoridated ( $\leq 1$ ppm), to inhibit dental cavity formation, elevated fluorine concentrations ( >2 ppm) may cause fluorosis; in warm climates lower concentrations may pose problems (Minoguchi, 1977). Fluorite in greisen and fluorite-beryllium zones associated with tin skarns may provide geoavailable fluorine and beryllium.

### Soil, sediment signatures prior to mining

The geochemical database for the Tonopah 1°x2° quadrangle, Nev., showed strong anomalies in Ag, As, Bi, Cd, Cu, Mo, Pb, Sb, W, and Zn in many places. The lead-zinc-antimony-arsenic signature appears to be associated with cross-cutting polymetallic veins peripheral to associated skarn deposits (Nash, 1988). Stream sediment samples from drainages associated with this deposit type have geochemical signatures that are similar to those of ore samples, but contain lower concentrations due to dilution. In the Great Basin, sedimentary transport causes scheelite to mechanically disintegrate to very fine grain sizes within about 3 km of its source.

### Potential environmental concerns associated with mineral processing

Processing tungsten and tin ore probably poses fewer problems than those associated with most other ore types. No tungsten compounds are included as toxic substances on U.S. Environmental Protection Agency (EPA) toxic release inventory lists (Smith, 1994). However, elevated fluorite abundances associated with some tin skarn deposits suggest that particulate emissions may pose environmental hazards.

Smelter signatures

The preferred method of tin ore beneficiation (fuming, smelting, or refining) depends on tin grade and content of iron and other impurities (Bleiwas and others, 1986). Fuming and smelting may release sulfur and arsenic.

Climate effects on environmental signatures

The effects of various climatic regimes on the geoenvironmental signature specific to these deposits are not known. Because most of these deposits have relatively low sulfide mineral contents and because carbonate minerals that have abundant acid consumption potential are abundant in association with these deposits, environmental signatures associated with tin and (or) tungsten skarn and replacement deposits are probably not much affected by climatic regime variation. Both scheelite and cassiterite are resistant minerals and their tungsten and tin contents are relatively immobile within a range of surficial weathering regimes.

Geoenvironmental geophysics

For those deposits where sulfide mineral oxidation may present hazards, induced polarization surveys can provide an estimate of sulfide mineral abundances in unmined ore or in solid mine waste. A combination of induced polarization, electromagnetic, and direct-current resistivity surveys can help trace the source and flow of acid water associated with sulfide mineral oxidation. Although no longer commercially available, the airborne UV-laser induced fluorescence method (Luminex) provides a rapid and sensitive method that may have application to identification of dispersed waste trains via direct scheelite identification.

Remote sensing methods can delineate the extent of altered rock and define iron oxide mineral distributions. Plant density variations and growth vigor (stress) related to metal release and smelter plumes can be delineated with multispectral reflectance imaging methods, but stress caused by toxic elements or acid drainage and that from lack of water or other factors cannot be distinguished. New applications of airborne imaging spectroscopy data from NASA's Airborne Visible and Infrared Imaging Spectrometer may hold great potential for mapping environmental contamination on a regional scale by identifying surface distributions of various minerals on the basis of reflectance differences due to slight changes in chemistry and crystal structure (Clark and others, 1993; King and others, 1994).

Effects of metals associated with these deposits types on life

Plants: Tin is not a known plant nutrient, but is known to become concentrated in plants growing in tin-enriched soil.
Animals: Animal studies suggest that ingested tungsten is either nonabsorbed and excreted or rapidly excreted and of the trace elements identified in coal, tungsten is the least toxic to a variety of fish species (Smith, 1994).
Humans: Tungsten is not known to be toxic to humans (no documented cases of tungsten poisoning) and no tungsten compounds have been included in the EPA's toxic release inventory list (Smith, 1994).

PERSPECTIVE

See section entitled "Perspective" in CU, AU, ZN-PB skarn deposits model (Hammarstrom and others, this volume).

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